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ORGANIC COMPOUNDS OF INDUSTRIAL ORIGIN IN THE ST. CLAIR RIVER

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Ministry
of the
Environment

The Honourable
George A. Kerr, Q.C.,
Minister

Everett Biggs,
Deputy Minister

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ORGANIC COMPOUNDS OF INDUSTRIAL ORIGIN IN THE ST. CLAIR RIVER

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SUMMARY

Considerable progress has been made in Ontario in the control of both inorganic and organic substances arising from industrial operations. However, the presence of trace quantities of specific organic substances is of concern and must be investigated to determine their impact on receiving water quality.

This work is the first part of a program aimed to provide further information on trace amounts of specific organic materials of industrial origin in the aquatic environment in Ontario. The identification and quantitation of organic compounds in the receiving waters contributes to the proper assessment of the effects of industrial activities on the quality of water and may also permit the identification of problem sources. The St. Clair River at Sarnia was selected for this investigation since the surrounding area contains one of the highest concentration of chemical manufacturing industries in the Province.

In the first phase of the project, industrial effluents and some industrial intake waters were sampled at 26 sites. After a preliminary screening (extraction and gas chromatography), selected samples were analyzed by gas chromatograph/mass spectrometry (GC/MS). A total of 47 organic compounds were identified. These can be classified in four major groups: Organohalides (21); Aromatic hydrocarbons (12); Alcohols and Carbonyl compounds (8); Aliphatic hydrocarbons Alkenes and Acetylenes (4); and others (2). In the second phase 23 locations were re-sampled and the effluents were analysed both qualitatively (GC/MS identifications) and quantitatively by gas chromatography to obtain data on the concentrations or estimated levels of 26 individual organic compounds. The levels of organic compounds quantitated were generally low. Analysis of sediment samples collected from the St. Clair River in the vicinity of industrial outfalls indicated that organic contaminants tend to accumulate in the sediments giving solvent extractable residues in the 300 - 5,000 mg/kg range. These results identified sediments as a prime area for future, more detailed investigation.

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INTRODUCTION

Problems associated with organic environmental contaminants surfaced several years after the persistent insecticides such as DDT received widespread usage. The stability of these compounds, considered a desirable property for their application, resulted in unexpected and far-reaching consequences. Being resistant to biological degradation, these compounds passed unchanged or slightly altered chemically through the food chain, accumulating to dangerous concentrations in the process. With the development of very sensitive analytical methods, a large number of organic compounds, pesticides and related products (such as PCBs) in the environment are routinely analysed today and their ecological effects are the subject of intensive investigation.

Organic compounds in industrial effluents present a special challenge to environmental scientists. From this source, thousands of known and unknown compounds enter the aquatic environment and can undergo a series of complex transformations, reacting with each other, with water and inorganic compounds, or be metabolized by living organisms of all forms. The original pollutants and their derivatives can have an immediate effect on aquatic life and may influence global ecology on a long term basis. Naturally, human health is also affected by this process. Previous work has demonstrated that industrial waste materials or products present in raw water can break through conventional water purification systems and appear in drinking water. Some organic compounds may break down after chlorination and form halogenated hydrocarbons such as chloroform, dichlorobromomethane and dibromochloromethane, contaminating finished drinking waters.

In the past, attempts to identify trace organics in water generally failed owing to the lack of suitable analytical methods and technology.

In recent years a number of instruments and techniques were developed which permit the isolation and identification of organic compounds even at the very low levels generally encountered in the aquatic environment. Among the new techniques, a very effective analytical system was developed by interfacing a gas chromatograph, a mass spectrometer and a computer (electronic data processing and instrument control). This GC/MS/EDP, system, combined with the necessary

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scientific expertise, is capable of identifying and often simultaneously quantitating trace components of complex mixtures. Compounds which do not lend themselves to gas chromatographic separation may be isolated by other techniques and then identified by mass spectrometry. Other methods of instrumental analysis, such as infrared and nuclear magnetic resonance spectroscopy may also provide valuable complementary information concerning the nature and identity of organic materials.

The Laboratory Services Branch of the Ontario Ministry of the Environment brought on-line the operation of a GC/MS/EDP system during 1975 and commenced the investigation of organic chemicals in industrial effluents. The highly industrialized Sarnia area along the St. Clair River was chosen as the first target for investigation. In this preliminary study, efforts were concentrated on the volatile or less soluble and therefore more readily extractable organic compounds. Even with these limitations, positive identification was made of some 47 organic compounds discharged to the St. Clair River.

EXPERIMENTAL

SAMPLING:

A. Samples for pre-screening and identification

Duplicate 32 oz grab samples were obtained from the effluents of ten industries located along the St. Clair River in the Sarnia area. Samples were also obtained from the effluents of the different process units at selected sites. All samples were stored at 5° in tightly capped (aluminum foil-lined screw caps) 32 oz sample bottles until analyzed.

B. Samples for quantitative analysis

Samples of industrial effluents from two major industries and three other sources were collected and stored as above. Samples for vinyl chloride analysis were collected separately in 20 ml hypo-vials and sealed immediately after sampling with Teflon lined butyl rubber septa.

C. Sediment Samples

Sediment samples were collected from the top 2-3 cm layer at Sarnia Bay and downstream above and below selected industrial outfalls. The samples were transported and stored in 16 oz. sediment jars provided with aluminum lined screw caps.

INSTRUMENTATION

The pre-screening of solvent extracts was carried out using a Hewlett Packard 7600 gas chromatograph equipped with a flame ionization detector. The GC/MS/EDP system employed in this study consisted of the following components:

Gas Chromatograph:	Hewlett Packard 7600
Mass Spectrometer:	Double-beam A.E.I. MS-30
Electronic data processor:	Data General Nova II Computer Tektronix 4010 visual display terminal Tektronix 4610 hard copy unit

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Infrared spectra of sediment extracts were recorded with a Beckman 4240 infrared spectrophotometer.

The gas purging apparatus was specially constructed to our specifications and is shown in Figure 2.

PRE-SCREENING OF SAMPLES

The total of over 50 duplicate samples would have required far too much time for GC/MS/EDP analysis and therefore a screening procedure was adopted. One of each of the duplicate samples were extracted with cyclohexane and the extracts were concentrated in a slow stream of nitrogen gas at below 30^{o} to approximately 1 ml. These extracts were obtained from each sample at pH 7, pH 1 and pH 11, respectively, using three times 15 ml portions of cyclohexane for each extraction. The concentrated extracts were then analysed by gas chromatography. The duplicates of samples showing significant organic content by this screening were then analysed using the GC/MS/EDP system. It was estimated that the solvent extraction technique would have indicated the presence of organic contaminants at concentrations of 200 ug/l or above in the original sample.

For the gas chromatographic analysis (flame ionization detector) 5 ul aliquots of the concentrated extracts were injected onto a 6' x 1/8" all glass column packed with 3% UCW-98 on Chromosorb W (80/100 mesh) which was temperature programmed from 60^{o} to 200^{o} at 10^{o}/min.

IDENTIFICATION OF ORGANIC COMPOUNDS

Samples for identification work were selected on the basis of screening results. The gas purging procedure applied is illustrated in Figure 2. Sample aliquots (500 ml) were placed in the gas purging vessel, immersed in a 90^{o} water bath, then purged with nitrogen (15 ml/min) with simultaneous magnetic stirring, for 20 minutes. The volatilized organic compounds were collected on a 1 ft. long Dexsil-300 and Tenax-GC trap. The trap was then transferred to the GC oven of the GC/MS/EDP system (see Figure 3) for analysis. The GC conditions were identical to those used in the screening procedure.

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During the analysis, the MS/EDP system acquired one complete mass spectrum every five seconds. This rapid acquisition of mass spectra allowed the identification of even only partially separated components. Simultaneous monitoring of the total ion current during analysis furnished a mass chromatogram, the equivalent of a gas chromatogram in a normal GC analysis. In Figure 4, a mass chromatogram of the purged organics from one of the effluent samples is shown, indicating the presence of 11 components. Figure 1 illustrates the mass spectrum of a typical chlorinated hydrocarbon (carbon tetrachloride) and Figures 5 - 14 show the mass spectra of some of the organic compounds identified in this study.

QUANTITATIVE ANALYSIS OF EFFLUENT SAMPLES

Samples collected for quantitative analysis were first analysed by GC/MS using the purging method described earlier, identifying the organic compounds present. The duplicates and triplicates were used for quantitation by gas chromatography. Quantitative analysis was carried out in four separate operations, one for each specific group of organics or vinyl chloride.

GROUP A., VOLATILE ORGANOHALIDES

This group included chloroform, dibromochloromethane, dichlorobromomethane, trichloroethylene and carbon tetrachloride. Analysis of these compounds was carried out by direct aqueous injection. The method was described in detail in an earlier report (Organics in Ontario Drinking Waters, Part 1. The Occurrence and Determination of Free and Total Potential Haloforms, by A.A. Nicholson and O. Meresz, 1976). Results are given in Table 4.

"GROUP" B., VINYL CHLORIDE

Samples for vinyl chloride analysis were collected separately in 20 ml hypo-vials. The head space gases were analysed using an 1/8" x 7', 0.4% Carbowax 400 column operated isothermally at 100^{o} (flame ionization detector). The detection limit with this method is 1.0 ug/l vinyl chloride in water. The results are shown in Table 4.

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GROUP C. ALCOHOLS

Alcohols were quantitated by direct aqueous injection using an 1/8" x 6' Porapack Q column, temperature programmed from 90°C to 250° at 8°/min and a flame ionization detector. Calibration curves were determined for the following alcohols: methanol, ethanol, i-propanol, n-butanol, i-butanol, t-butanol, n-pentanol, i-pentanol and 3-pentanol. These alcohols could be detected at 1.0 mg/l. However, only ethanol, i-propanol and t-butanol were found in some of the samples analysed,(Table 5).

GROUP D., AROMATIC HYDROCARBONS

Benzene, toluene, xylenes, ethylbenzene and styrene were quantitated. The sample (900 ml) was extracted with 1.0 ml of hexane and the extract was analysed on a 1/8" x 22' 5% Bentone- 34/5% DIDP column, operated isothermally at 125°. The detection limit using a flame ionization detector was 1.0 mg/l. The results are shown in Table 5.

GROUP E

This group included eight organohalides and four other organics which were not determined separately. Their levels in the industrial effluents investigated were estimated on the basis of the flame ionization chromatograms recorded during GC/MS analysis. As shown in Table 6, all levels were below the 1 mg/l range and estimated to vary between 10 ug/l and 100 ug/l.

SEDIMENT ANALYSES (SOLVENT EXTRACTABLES)

Aliquots (20 g) were mixed with anhydrous magnesium sulphate (20 g) and extracted in a Soxhlet extractor with chloroform for 4 - 6 hours (40 cycles). The extracts were evaporated on a steam bath. The residues were weighed. The amounts of solvent extractables were calculated on the basis of sediment dry weight following moisture determination on another aliquot. Results are listed in Table 7.

The organic residues obtained were also investigated by infrared spectroscopy as liquid films on sodium chloride discs using a Beckman 4240 infrared spectrophotometer.

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SEDIMENT ANALYSIS BY GAS CHROMATOGRAPHY - MASS SPECTROMETRY

Sediment samples (100 g) were suspended in water (100 ml), purged and analysed by GC/MS as described for the water samples above. Results are shown in Table 8.

RESULTS AND DISCUSSION

A total of 26 sites were sampled in the Sarnia area. These were mainly industrial outfalls, but one test well near a dump site and two raw industrial water intakes were also included.

There were 47 organic compounds identified during the study. The compounds identified and the frequency of their occurrence are listed in Table 2. Table 1 contains the results of extractive prescreening described in the experimental section. In Table 3, detailed information is given about the organic content of each individual effluent.

The organics found can be classified in five major groups:

(a) Organohalides (21)
(b) Aromatic hydrocarbons (12)
(c) Alcohols, Carbonyl Compounds (9)
(d) Aliphatic hydrocarbons, Alkenes, Acetylenes (4)
(e) Others (2)

One raw water (at the intake point) showed the presence of vinyl chloride while the other intake water contained, in addition to vinyl chloride, three other chlorinated hydrocarbons.

In general, the high number of organohalides (21) and especially the widespread appearance of vinyl chloride (11 sites) give rise for concern. However, it must be recognized that the appearance of vinyl chloride at all of the sampling points found cannot be explained on the basis of known potential sources and, therefore, more investigation is required to evaluate the significance of this substance in waste water and river water.

Considering that industrial effluents were investigated, levels of organic contaminants as shown in Tables 4, 5 and 6 are not unreasonably high. Tertiary butanol was present in one effluent (K-1), at the highest concentration of any of the organics identified (376 mg/l).

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While this alcohol is relatively non-toxic, it can cause fish tainting. Carbon tetrachloride had the second highest concentration of all the pollutants identified, and it was present in 15 of the 23 sources analysed quantitatively (Table 4).

The results of this study indicates that toxic chemicals are being released into the St. Clair River. However, the data at hand are insufficient to estimate the environmental impact of this contamination. Process fluctuations are experienced by most of the industries and hence the organic chemical content of their effluent may vary considerably with time and season. This is illustrated by effluent F-2 (Table 1) which when sampled during May, 1975, showed no measurable organics present, but when resampled in June (F-2a), contained more than traces of organic compounds.

The data reported here should be interpreted in light of the average daily effluent outputs by various industries, the toxicity, stability and possible bio-accumulation of the identified and quantitated organics as well as the dilution rate in the river. The average flow rate of the St. Clair River is estimated at 220,000 cfs (about six million litres per second). In spite of this high dilution factor, it appears that organic chemicals do accumulate in the sediments, especially in the vicinity of industrial outfalls. This is well illustrated by the variations in the levels of solvent extractables as shown in Table 7. Infrared spectrophotometric examination of the sediment extracts showed an organic profile comprising of a general background of very aged heavy petroleum hydrocarbons upon which the characteristic spectral features of alkyl substituted aromatic hydrocarbons are superimposed whenever the total solvent extractable values approach or rise above 1000 mg/kg. It should be pointed out that the infrared technique is relatively "blind" to organohalides and these may also be present together with the aromatic hydrocarbons. Indeed, an exploratory GC/MS analysis of sediment samples showed the presence of organohalides (Table 8) and at one location these were present at high concentrations (Table 9).

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RECOMMENDATIONS

In light of the present study, the following recommendations are made:

1. That qualitative and quantitative monitoring of industrial effluents for organic compounds be continued using composite rather than grab samples.
2. That the study be extended towards the detection of water soluble polar organic compounds which were not considered during the exploratory work.
3. That effluents and intake waters be monitored for vinyl chloride and carbon tetrachloride content.
4. That efforts be made to interpret available data (TOC, BOD and COD) on daily effluent outputs considering the findings of the present study. It would be of particular importance to examine whether the highly halogenated organic compounds such as carbon tetrachloride chloroform and trichlorethylene are reflected in TOC measurements.
5. That similar studies be carried out in other industrialized areas.
6. That chemical identification work be complemented by toxicological studies (on fish) with special attention to possible synergistic effects.
7. That the analysis of sediments for organic contaminants be considerably extended in the future.
8. That research projects be funded to evaluate the retention of lower molecular weight organics by river and lake sediment and, the effects of sediments contaminated by organics of industrial effluent origin on benthic fauna (toxicity, mobilization).

TABLE 1

PRELIMINARY SCREENING OF EFFLUENTS FOR ORGANICS BY EXTRACTION AND GAS CHROMATOGRAPHY

EFFLUENT	EXTRACT		
	NEUTRAL	ACIDIC	BASIC
A-1	-	-	-
A-2	-	trace	trace
A-3	-	-	-
B-1	-	-	-
B-2	-	*	*
B-3	-	*	*
B-4	trace	trace	*
B-5	*	-	trace
C-1	*	*	trace
C-2	trace	*	trace
C-3	*	*	trace
C-4	trace	trace	trace
C-5	trace	trace	-
C-6	*	*	*
C-7	-	trace	trace
C-8	trace	*	*
C-9	trace	trace	trace
C-10	trace	trace	trace
D-1	trace	trace	-
D-2	-	-	-
D-3	trace	trace	trace
E-1	-	-	-
E-2	-	trace	trace
E-3	*	*	-
E-4	-	-	-
F-1	-	-	-
F-2 7/5/75	-	-	-
F-2a 6/6/75	*	-	trace
G-1	*	-	trace
G-2	-	trace	trace
G-3	trace	trace	trace
G-4	trace	trace	trace
G-5	-	-	*
G-6	-	trace	trace
G-7	trace	trace	trace

/............

TABLE 1 (Continued

EFFLUENT		EXTRACT		
		NEUTRAL	ACIDIC	BASIC
H-1		trace	-	-
H-2		*	-	*
H-3		*	-	*
H-4		-	-	-
H-5		-	-	-
I-1		trace	trace	trace
I-2		-	-	-
I-3		*	*	*
I-4		trace	trace	-
I-5		-	-	-
I-6		-	-	-
I-7		*	*	*
I-8	13/6/75	-	trace	-
I-8a	5/5/75	-	-	-
J-1		trace	-	-
J-2		-	trace	trace

- = None Detected

* = Measurable organics

TABLE 2

ORGANIC COMPOUNDS IDENTIFIED IN INDUSTRIAL EFFLUENTS ENTERING THE ST. CLAIR RIVER.

Group A) Organohalides

Compound.	No. of Sites Found
Ethyl Chloride	2
Vinyl chloride	11
Vinyl bromide	1
Chloro-propene	1
Dichloromethane	1
Dichloroethane	5
Dichloroethylene	2
Dichloropropane	6
Dichloropropene	1
Bromochloroethane	2
Dichlorobutadiene	1
Dibromomethane	2
Chloroform (trichloromethane)	10
Trichloroethylene	7
Trichloropropane	1
Tribromomethane (bromoform)	1
Carbon tetrachloride	1
Tetrachloroethane	5
Tetrachloroethylene	2
Hexachloroethane	1
Bis-2-chloroethyl ether	1

Group B) Aromatic Hydrocarbons

Benzene	3
Toluene	7
Xylenes	8
Propylbenzene	1
Diethyl benzene	1
Propyl toluene	1
Cumene	1
Sytrene	1
Naphthalene	3
Methylnaphthalene	3
6-Methyl-1,2-dihydronaphthalene	1
Benzocyclobutene or phenylacetylene	1

Group C) Ethers, Alcohols, Carbony/Compounds

Formaldehyde	1
Propanol	1
Tert.Butanol	1
Decanols	2
Octadecanol	1
But-2-en-1-ol	1
Acetone	2
Methyl ethyl ketone	1

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TABLE 3

ORGANIC COMPOUNDS IDENTIFIED IN INDIVIDUAL EFFLUENTS BY GC/MS USING THE GAS PURGING AND TRAPPING TECHNIQUE

EFFLUENT	COMPOUNDS IDENTIFIED
B-1	Vinyl chloride (trace)
B-2	Vinyl chloride
B-3	Vinyl chloride chloroform, dichloropropane,chloroethane
B-4	Vinyl chloride, chloroform, dichloropropane, trace of formaldehyde, N-(3,4-dichlorophyenyl)-N,N diethylurea
B-5	Vinyl chloride, benzene
C-1	Dichloromethane, chloroethane, dichloroethylene, dichloroethane, trichloro ethylene, tetrachloroethane, tetrachloroethene dichloropropane hexachloroethane, benzene, xylene
C-3	Large amount of tetrachloroethylene.
E-2	Dibromomethane, vinylchloride, vinyl bromide, chloroform, dichloroethylene, dichloroethane, trichloroethane, dichloropropane trichloropropane,toluene, xylenes benzocyclobutene/naphthalene, methyl-naphthalene
E-3	Dichloroethane, bromochloroethane tribromoethane, toluene propyltoluene, naphthalene,methylnaphthalene,6-methyl-1,2-dihydronaphthalene,
F-2	Vinylchloride, trace of toluene
F-4	Chloroform, vinylchloride, carbontetrachloride, trichloroethylene, trichloroethane, tetrachloroethane, dichloropropane, dichlorobutadiene, bis-(2-chloroethyl) ether
G-1	Octadecanol, decanols,
G-3	Chloroform, methylene bromide, trichloroethylene, cyclohexane, toluene, xylene
G-4	Chloroform, toluene, xylene
G-5	Chloroform, toluene, xylene
G-6	Chloroform, toluene, xylene,
G-7	Cyclohexane, toluene, xylene or ethylbenzene
G-8	Vinyl chloride, decanols.
I-1	Dichloropropane 5-n-butyl-4-nonene, hydrocarbons, decanes
I-2	Chloroform, bromochloromethane, vinylchloride, trichloroethylene dichloropropane, tetrachloroethane
I-3	Vinylchloride, dichloroethane, trichloroethylene, tetrachloroethylene.
K-1	Trichloroethylene, methyl-ethyl ketone, propanol, tert-butyl alcohol, but-2-en-1-ol.
K-2	Acetone, carbondisulphide, chloroform, xylenes or ethylbenzene cumene, diethylbenzene,
K-3	Vinylchloride, chloropropene
K-4	benzene, acetone, butene-3-yne, butadiene, styrene, naphthalene or divinylbenzene, methylnaphthalene, propylbenzene

TABLE 4

QUANTITATIVE ANALYSIS OF VOLATILE ORGANOHALIDES IN PLANT EFFLUENTS

EFFLUENT	ORGANOHALIDES ug/l					
	Vinyl chloride	Chloroform	Dichloro-bromomethane	Dibromo-chloromethane	Trichloro-ethylene	Carbon-tetrachloride
C-1	1	-	-	-	102	110
C-2	-	6	-	-	-	20
C-3	-	13	-	-	4	12
C-4	4	912	150	66	-	1390
C-5	-	70	21	-	-	13
C-6	13	-	-	-	-	1378
C-7	-	5	-		-	15
C-8	-	-	-	-	-	100
C-9	-	-	-	-	-	16
C-10	-	5	-	-	-	12
C-11	-	-	-	-	-	67
F-2	32	-	-	-	2	-
I-2	-	-	-	-	-	91
I-8	11	-	-	-	-	12
K-1	172	-	-	-	-	-
K-2	30	55	-	-	-	-
K-3	4	-	-	-	-	-
K-4	384	-	-	-	-	-
K-5	1	-	-	-	-	-
K-6	215	2	-	-	18	-
K-7	10	-	-	-	-	-

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TABLE 4 (Continued)

QUANTITATIVE ANALYSIS OF VOLATILE ORGANOHALIDES IN PLANT EFFLUENTS

EFFLUENT	Vinyl chloride	Chloroform	Dichloro-bromomethane	Dibromo-chloromethane	Trichloro-ethylene	Carbon-tetrachloride
M-1	-	-	-	-	-	19
M-2	-	202	-	-	-	981
Detection Limits*	1.0	1.0	0.5	1.0	2.0	1.0

* ug/l

TABLE 5

QUANTITATIVE ANALYSIS OF ALCOHOLS AND AROMATIC HYDROCARBONS IN PLANT EFFLUENTS

	ALCOHOLS mg/l			AROMATIC HYDROCARBONS mg/l				
EFFLUENT	Ethanol	t-Butanol	i-Propanol	Benzene	Toluene	Xylenes	Ethylbenzene	Styrene
C-1	-	-	-	-	-	*ppb	-	-
C-2	-	-	-	-	-	-	-	-
C-3	-	-	-	-	-	-	-	-
C-4	-	-	-	-	-	-	-	-
C-5	-	-	-	-	-	-	-	-
C-6	-	-	-	30	25	25	6	200
C-7	-	3	-	-	-	-	-	-
C-8	-	-	-	-	-	*ppb	-	-
C-9	-	3	-	-	-	-	-	-
C-10	-	3	-	-	-	-	-	-
C-11	-	-	-	-	-	*ppb	-	-
F-2	-	-	-	-	-	-	-	-
I-2	-	-	-	-	-	-	-	-
I-8	-	-	-	-	-	-	-	-
K-1	-	376	-	-	-	-	-	-
K-2								
K-3	-	7	4	-	-	-	-	-
K-4	47	-	-	149	12	5	-	-
K-5	-	-	-	-	-	-	-	-
K-6	-	-	-	-	-	-	-	-
K-7	-	-	-	*ppb	-	-	-	-
M-1	-	-	-	-	-	-	-	-
M-2	-	-	-	-	-	-	-	-

*ppb = Not quantitated, concentration estimated at the 10-100 ppb levels.

TABLE 6

LEVELS OF VARIOUS HYDROCARBONS AND ORGANOHALIDES IN PLANT EFFLUENTS EFFLUENTS AS ESTIMATED ON THE BASIS OF GC/MS IDENTIFICATION RUNS

+ = identified at 10-100 ug/l levels

- = none detected (less than 10 ug/l)

EFFLUENT	Butadiene	Diethylbenzene	Dimethyl-diethylbenzene	Diphenyl ether	Chloroethane	Dichloroethanes	Trichloroethane	Tetrachloroethane	Tetrachloro-ethylene	Dichloro-propane	Tetrachloro-propane	Hexachloro-butadiene
C-1		+	-	-	-	+	-	-	+	-	-	-
C-2	-					+	-	-	+			
C-3	-	+	-	-	-	+	-	-	+	+	-	-
C-4	-	-	-	-	-	+	-	-	+	-	-	-
C-5	-	-	-	-	-	-	-	+	+	+	+	+
C-6	-	+	-	+	-	-	-	-	-	-	-	-
C-7	-	-	-	-	-	+	-	-	-	-	-	-
C-8	-	+	+	+	-	+	-	-	+	-	-	-
C-9	-	-	-	-	-	+	-	-	+	-	-	-
c-10	-	+	+	-	-	+	-	-	+	-	-	-
C-11	-	-	-	-	-	+	-	-	+	-	-	-
F-2	-	-	-	-	-	+	+	-	-	-	-	+
I-2	-	-	-	-	-	-	-	-	-	-	-	-
I-8	-	-	-	-	-	-	-	-	-	-	-	-
K-1	-	-	-	-	-	-	-	-	-	-	-	-
K-2	-	-	-	-	-	-	-	-	-	-	-	-
K-3	-	-	-	-	-	-	-	-	-	-	-	-
K-4	+	-	-	-	-	-	-	-	-	-	-	-
K-5	-	-	-	-	-	-	-	-	-	-	-	-
K-6	-	-	-	-	+	+	-	+	-	-	-	+
K-7	-	-	-	-	-	-	-	+	-	-	-	-
M-1	-	-	-	-	-	-	-	-	-	-	-	-
M-2	-	-	-	-	-	-	-	-	-	-	-	-

TABLE 7

SOLVENT EXTRACTABLE ORGANICS IN ST. CLAIR RIVER SEDIMENTS

Lab Number	Code (Location)	Solvent Extractable mg/kg dry weight
0-3939	S	526
0-3940	SA	12,153
0-3941	SA-1	2,854
0-3942	SA-2	3,900
0-3943	SA-3	1,238
0-3944	SA-4	2,559
0-3945	SA-5	7,185
0-3946	SB-1	4,264
0-3947	SB-2	1,035
0-3948	SB-3	4,264
0-3949	SB-4	3,300
0-3950	SB-5	240
0-3952	SC	437
0-3953	SD	1,530
0-3955	SE	4,010
0-3956	SF	840
0-3957	SG-1	1,011
0-3958	SG-2	317
0-3959	SH	1,388
0-3960	SI	5,206
0-3961	SJ	2,738
0-3962	SK	211
0-3963	SL	591
0-3964	SM	364

TABLE 8

ORGANIC COMPOUNDS IDENTIFIED IN ST. CLAIR RIVER SEDIMENTS
(By Gas Purging and Gas Chromatography-Mass Spectrometry)

LOCATION	COMPOUNDS IDENTIFIED
SA-1	Dichlorobenzene
SA-2	Tetrachlorobutadiene Dimethylnaphthalene
SB-1	Tetrachloroethylene Hexachloroethane Pentachlorobutadiene Hexachlorobutadiene Dichlorobenzene Trichlorobenzene
SB-3	Tetrachloroethylene Hexachlorobutadiene Diethylbenzene Bromochlorobenzene
SB-4	Chloroform Carbon tetrachloride Trichloroethylene Tetrachloroethylene Hexachloroethane Hexachlorobutadiene
SE	Alkanes
SH	None
SI	None
SJ	Alkanes

TABLE 9

ORGANIC COMPOUNDS IDENTIFIED IN ST.CLAIR RIVER SEDIMENT SB-4 BY GAS PURGING AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY.

Compound	Approximate Concentration (mg/kg wet weight)
Carbon tetrachloride	200
Trichlorethylene	100
Tetrachlorethylene	400
Hexachlorobutadiene	50

Figure 1

MASS SPECTRUM OF CARBON TETRACHLORIDE

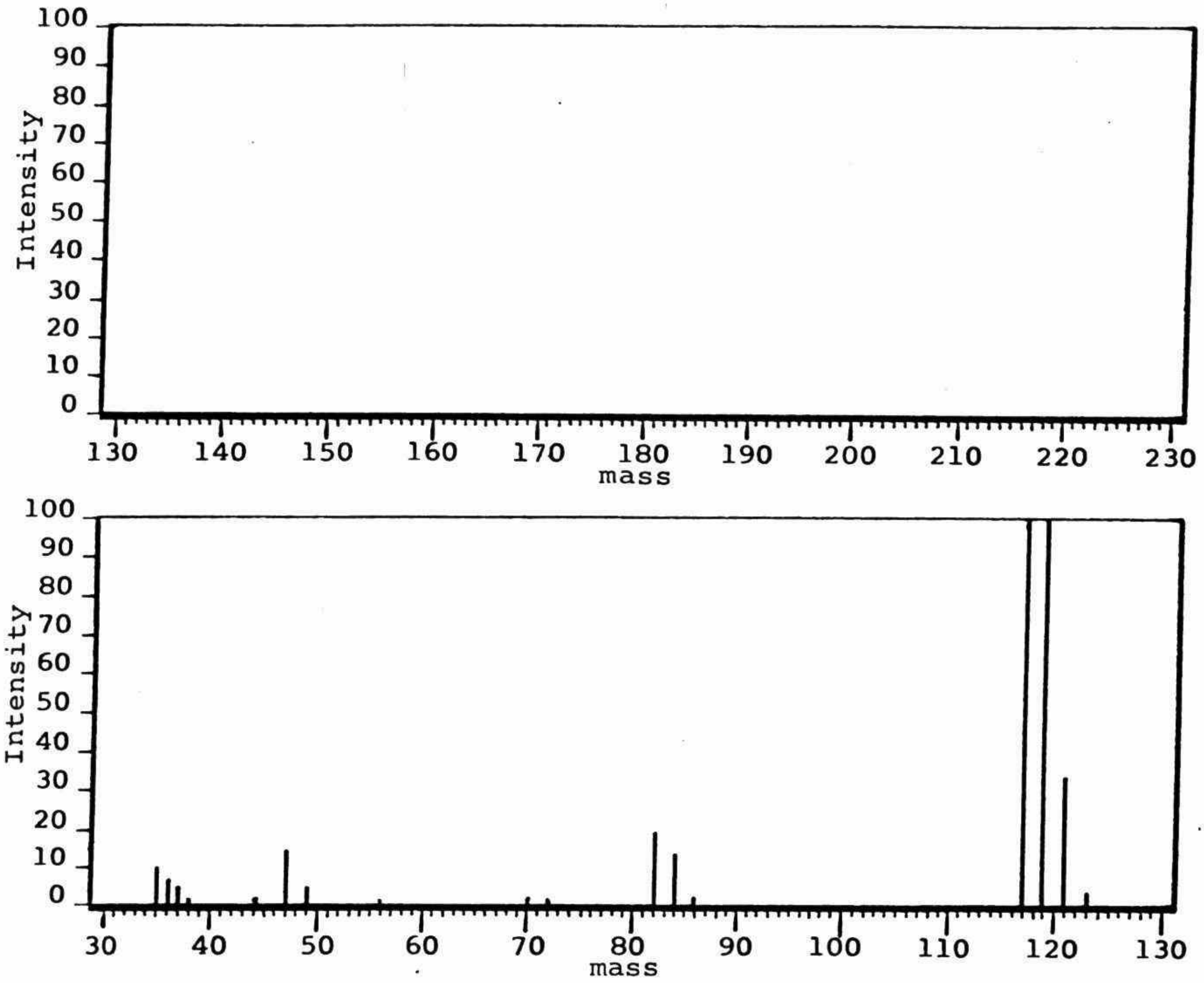


FIGURE 2

SCHEMATIC OF GAS PURGING APPARATUS

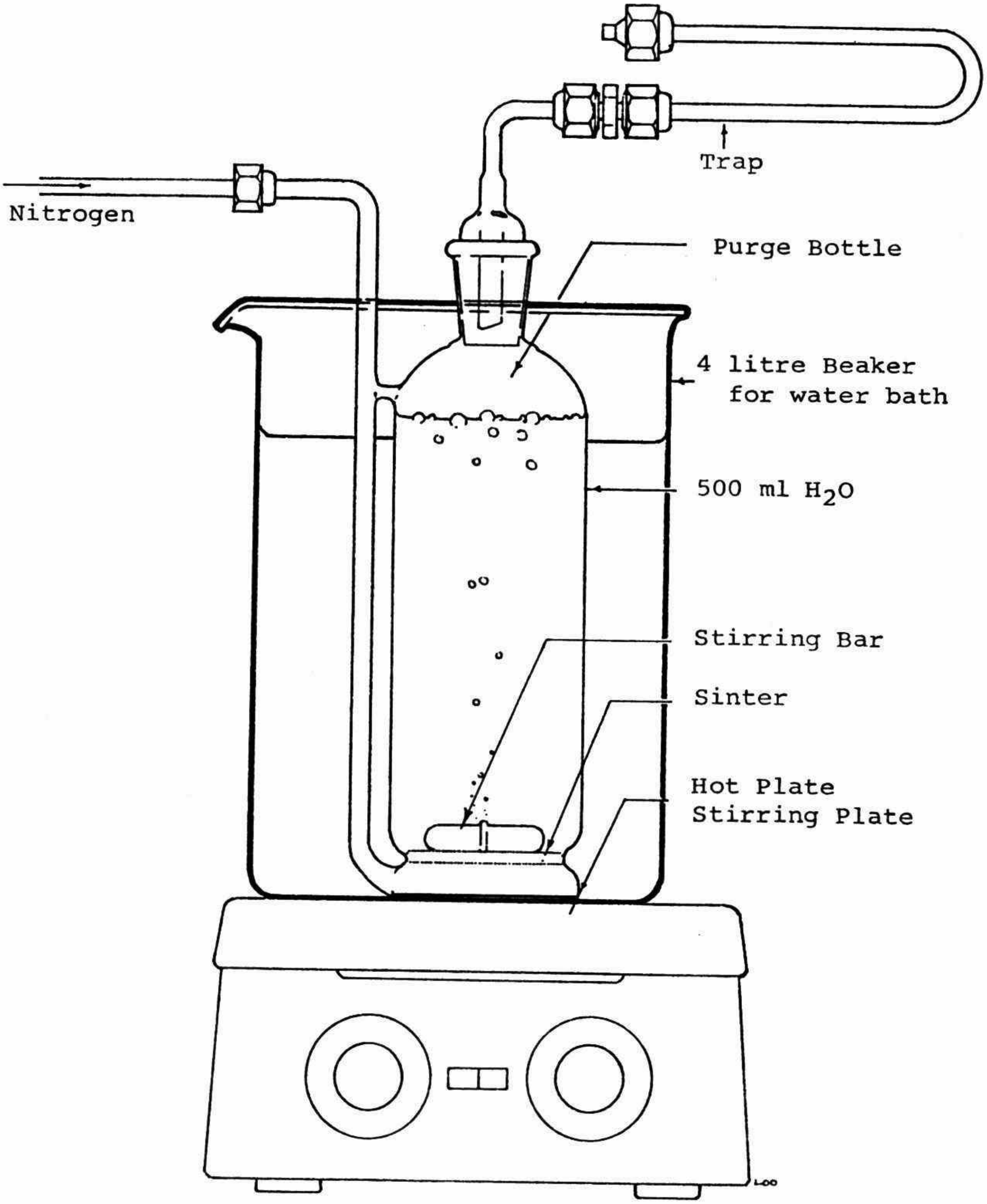


Figure 3

SCHEMATIC OF TRAP/CHROMATOGRAPH APPARATUS

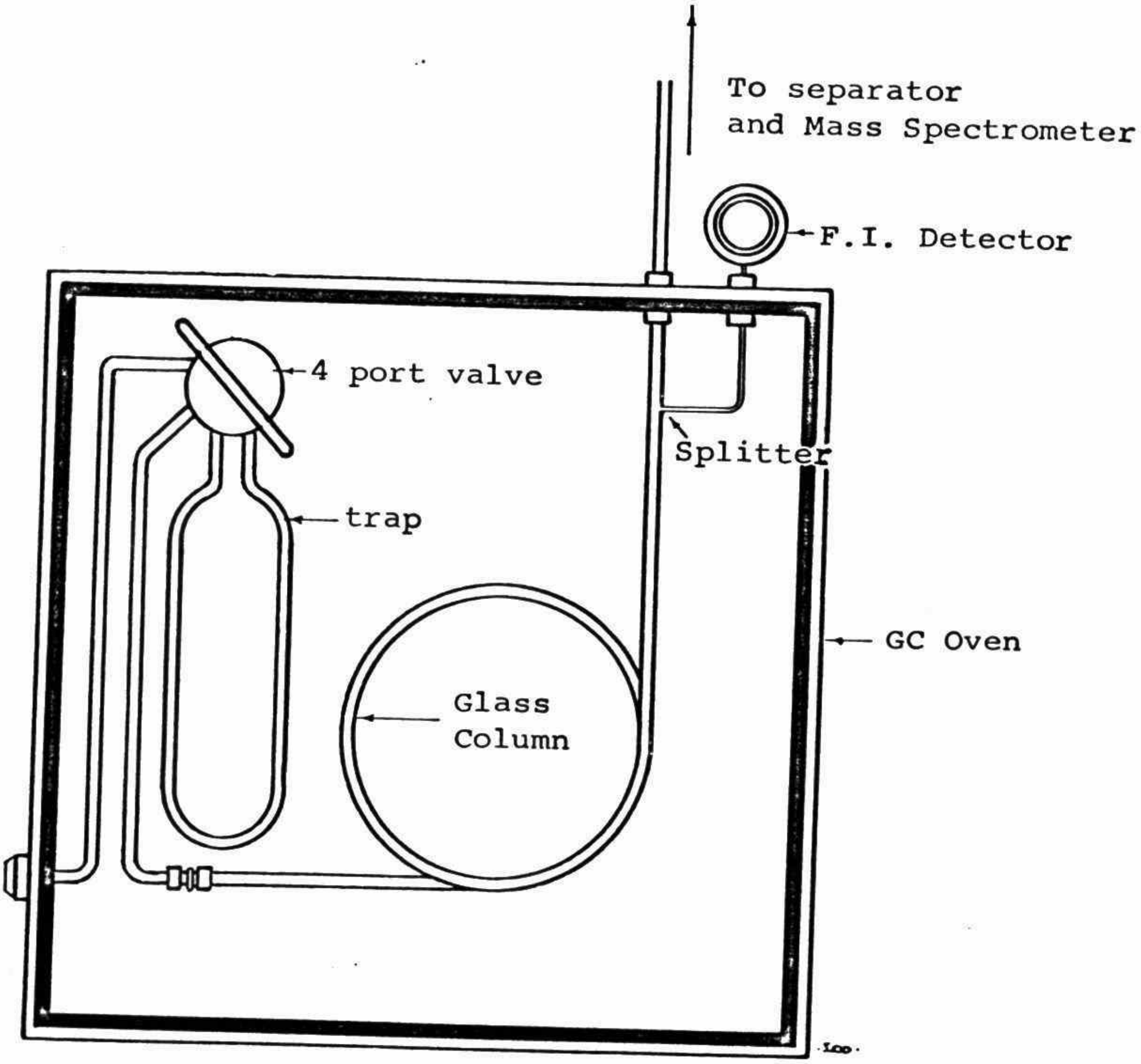


Figure 4

EXAMPLE OF A MASS CHROMATOGRAM OF AN INDUSTRIAL EFFLUENT

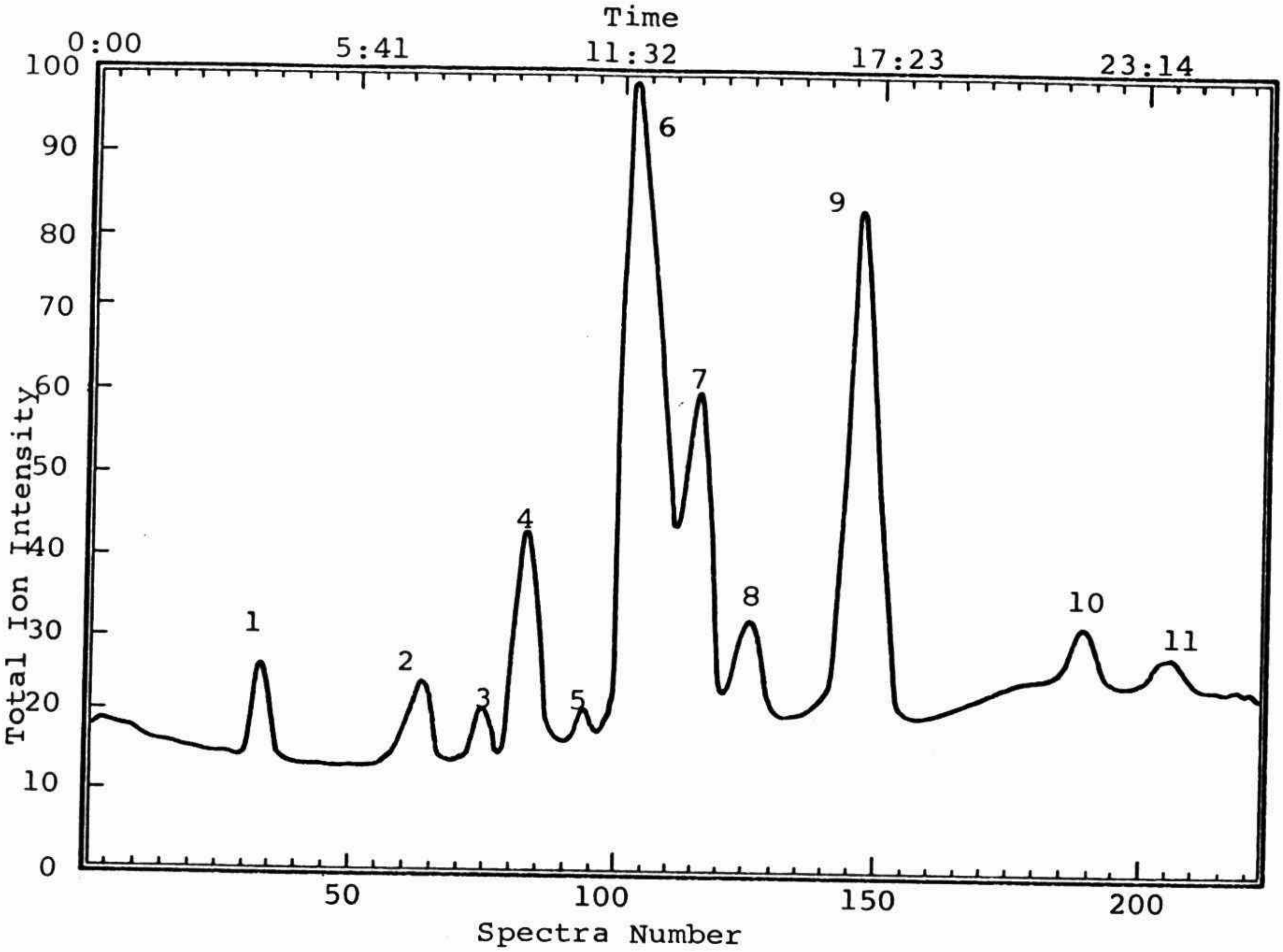
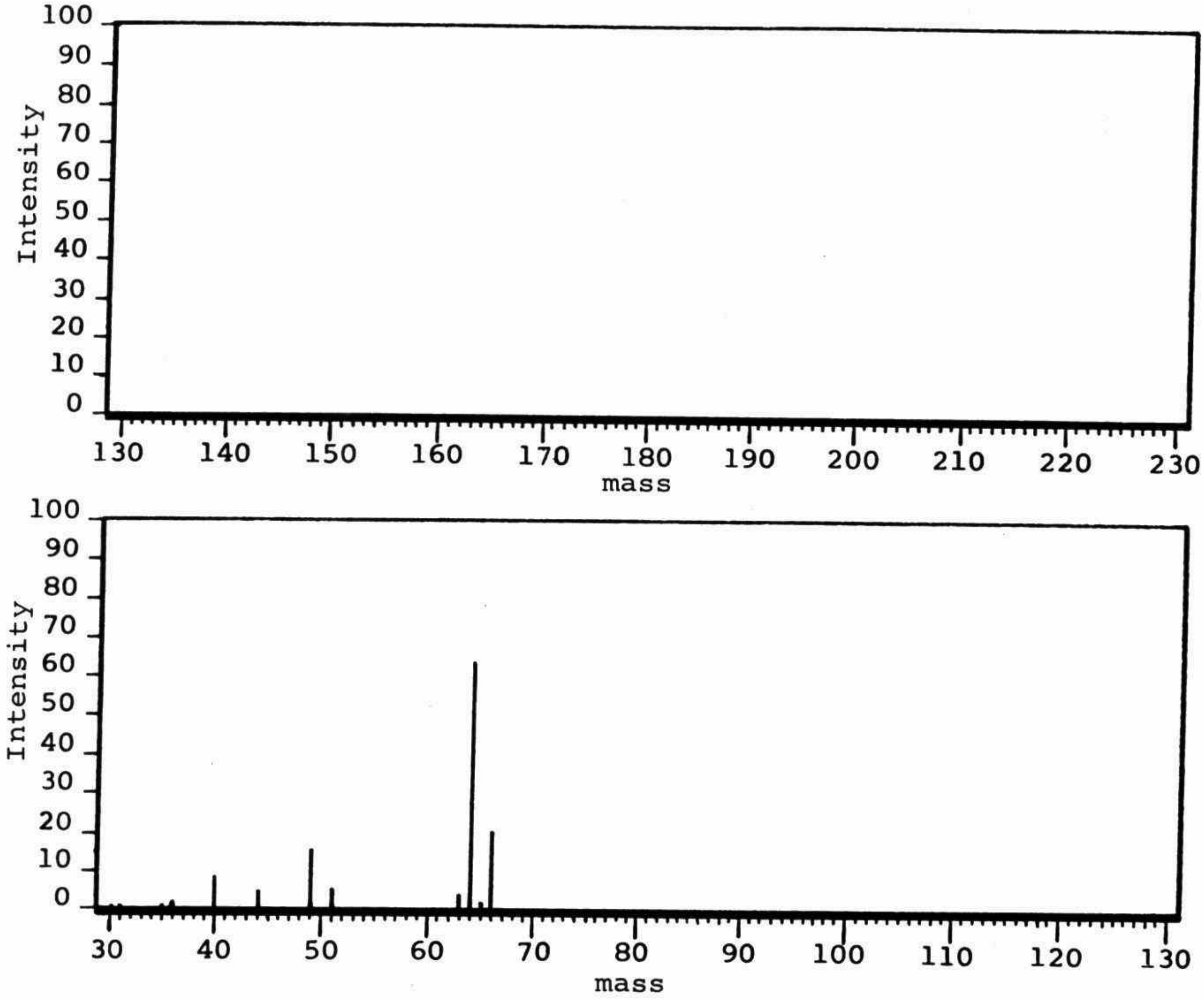


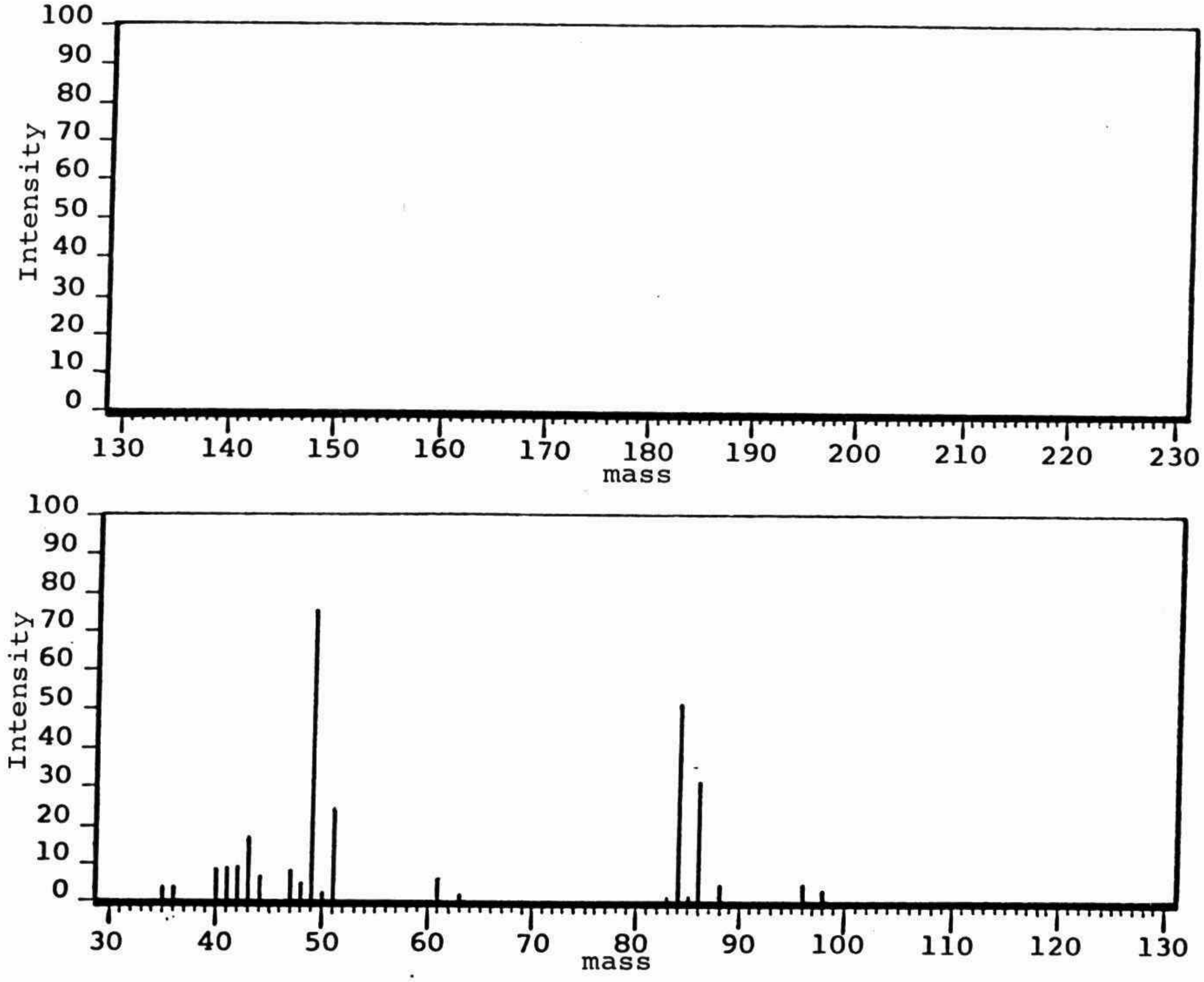
Figure 5: ETHYL CHLORIDE



Mass Chromatogram Peak 1

Spectrum No. 33

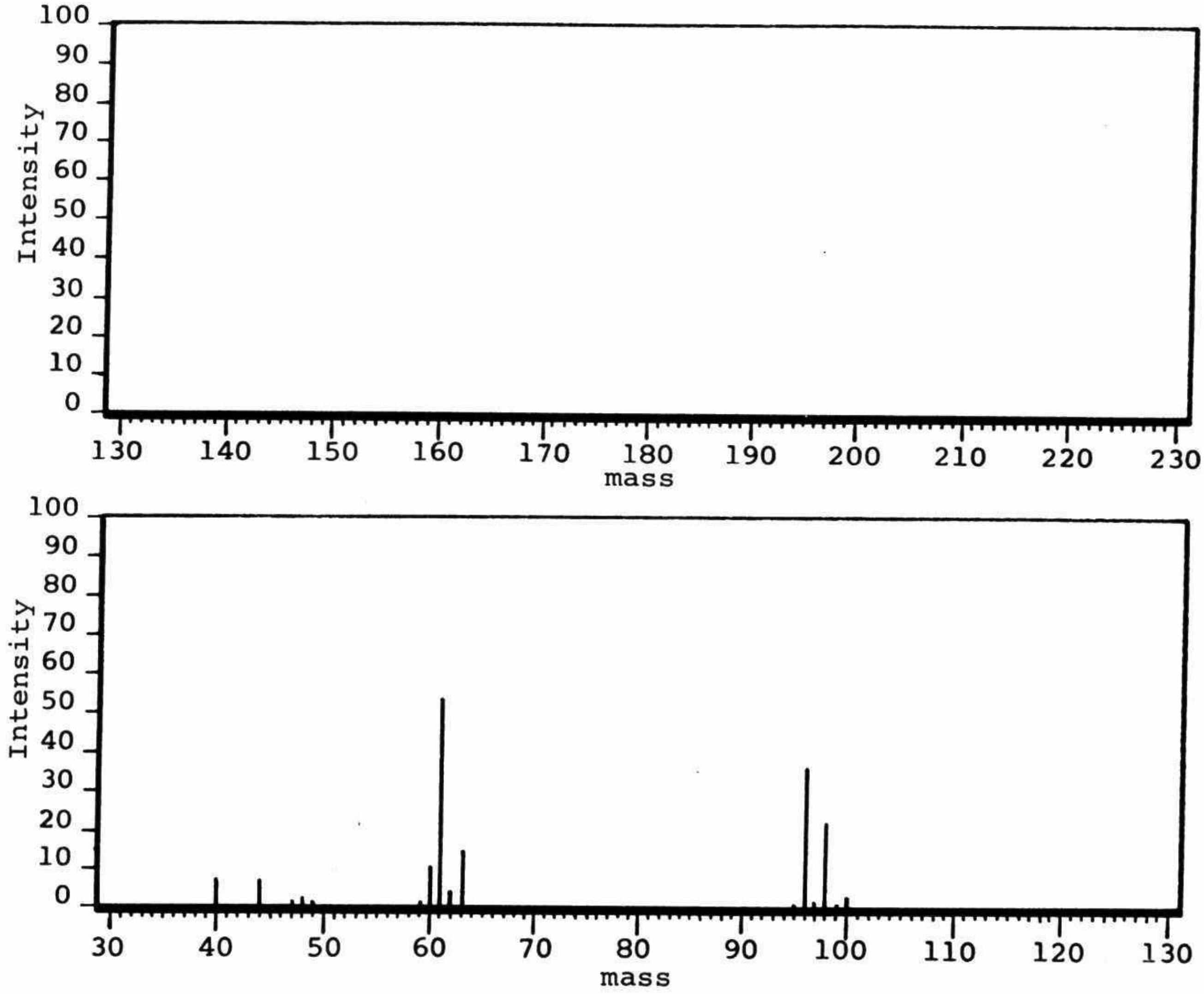
Figure 6: DICHLOROMETHANE



Mass Chromatogram Peak 2

Spectrum No. 63

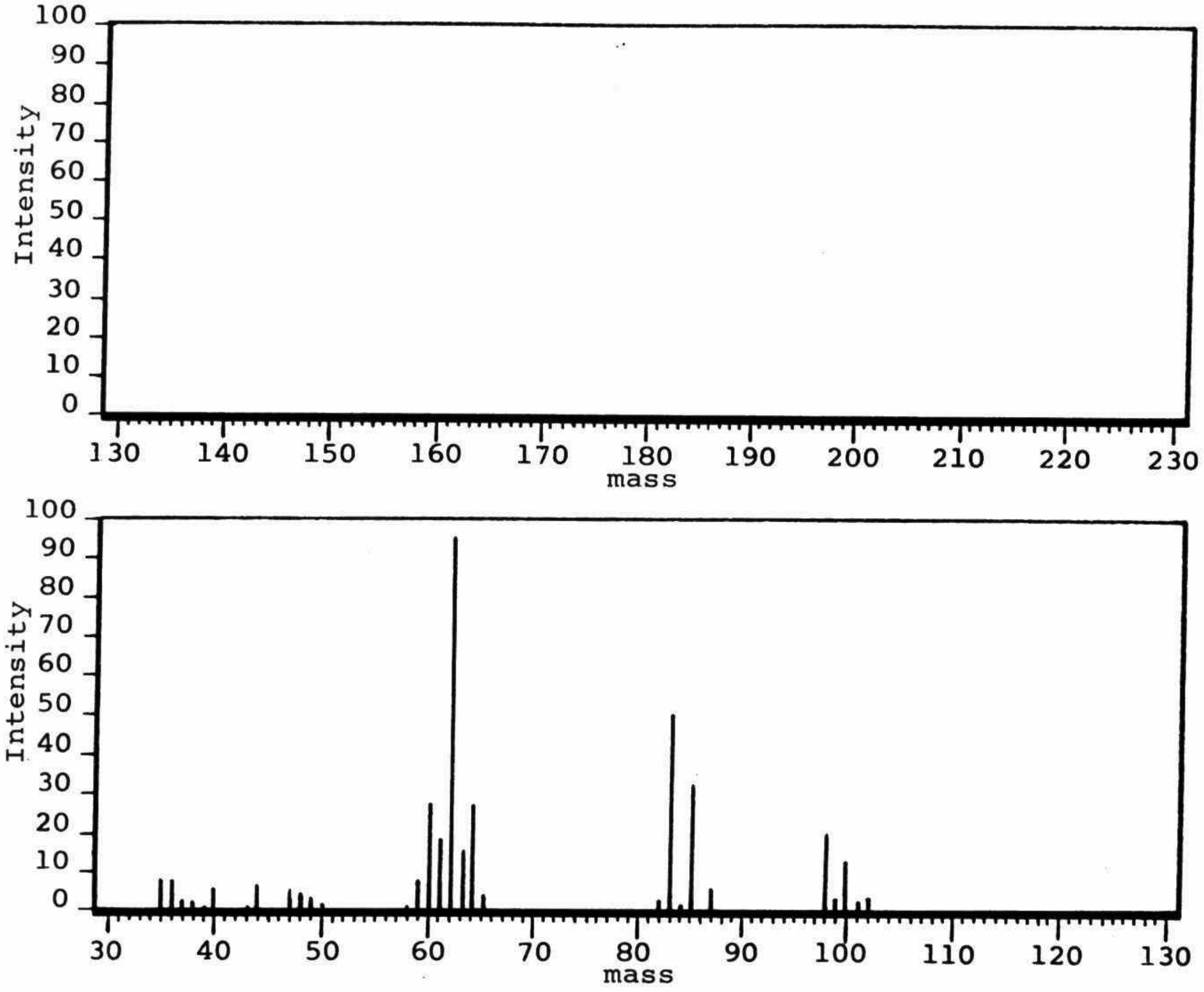
Figure 7: DICHLOROETHYLENE



Mass Chromatogram Peak 3

Spectrum No. 75

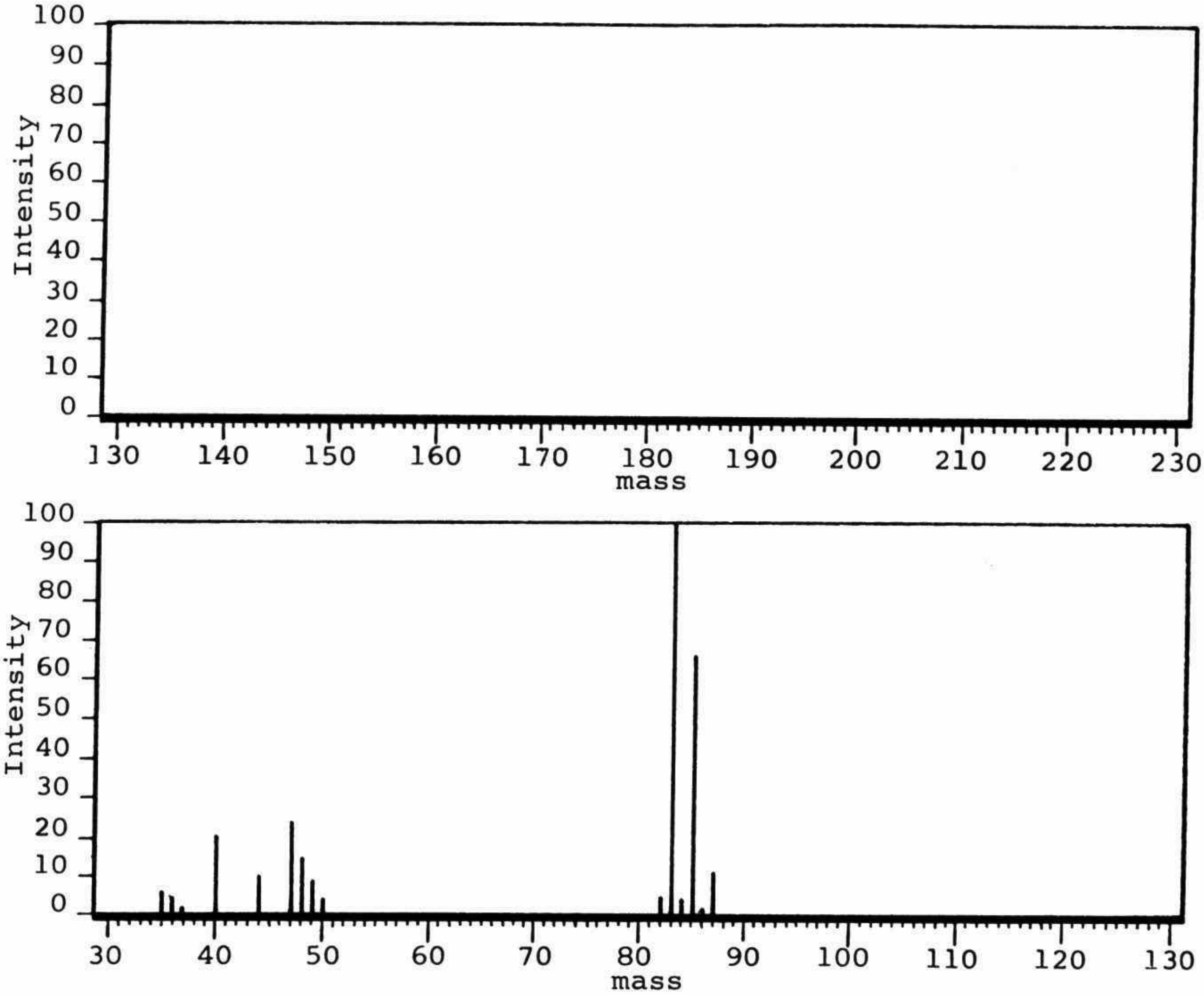
Figure 8: 1,1 DICHLOROETHANE



Mass Chromatogram Peak 4

Spectrum No. 82

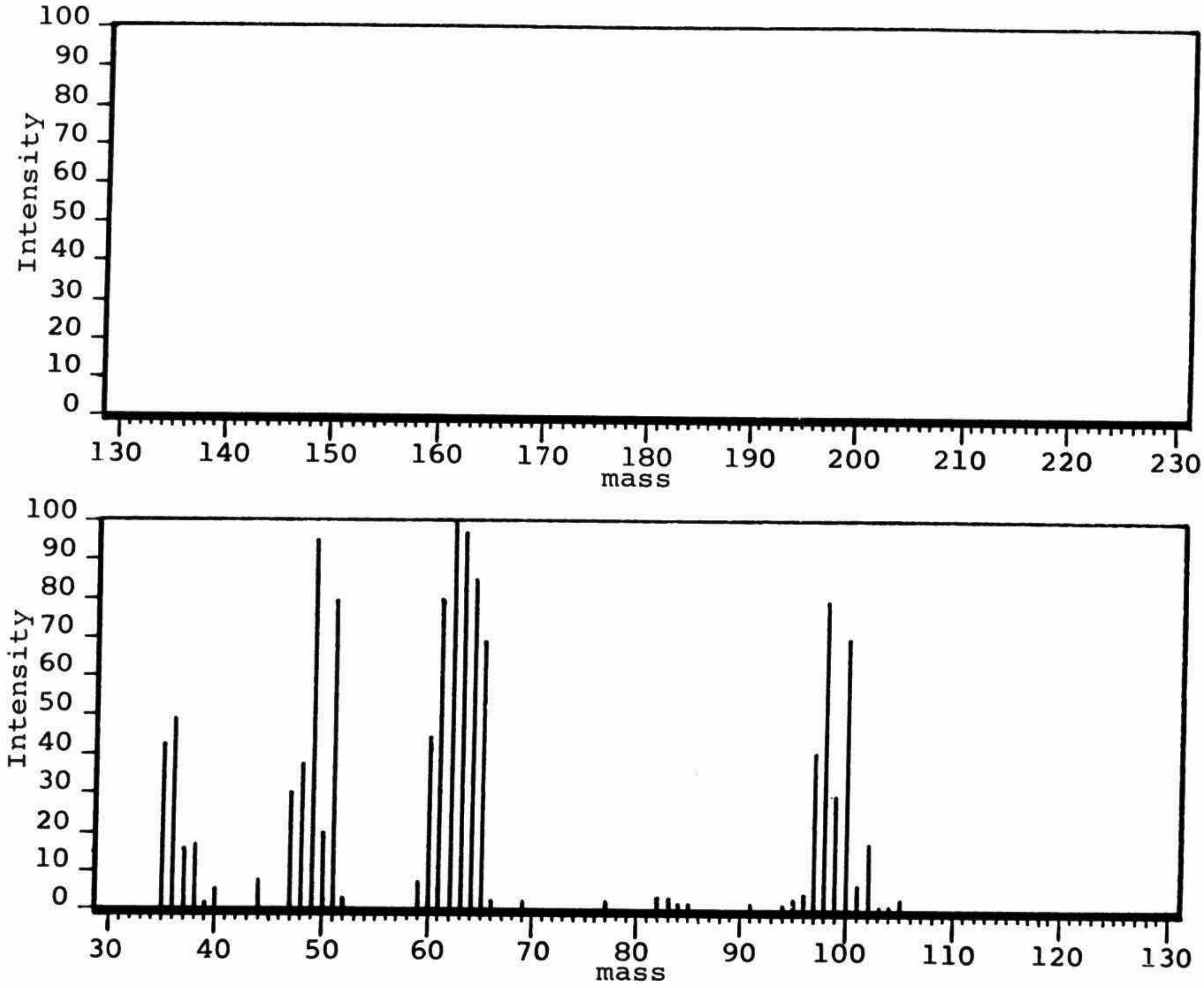
Figure 9: CHLOROFORM



Mass Chromatogram Peak 5

Spectrum No. 94

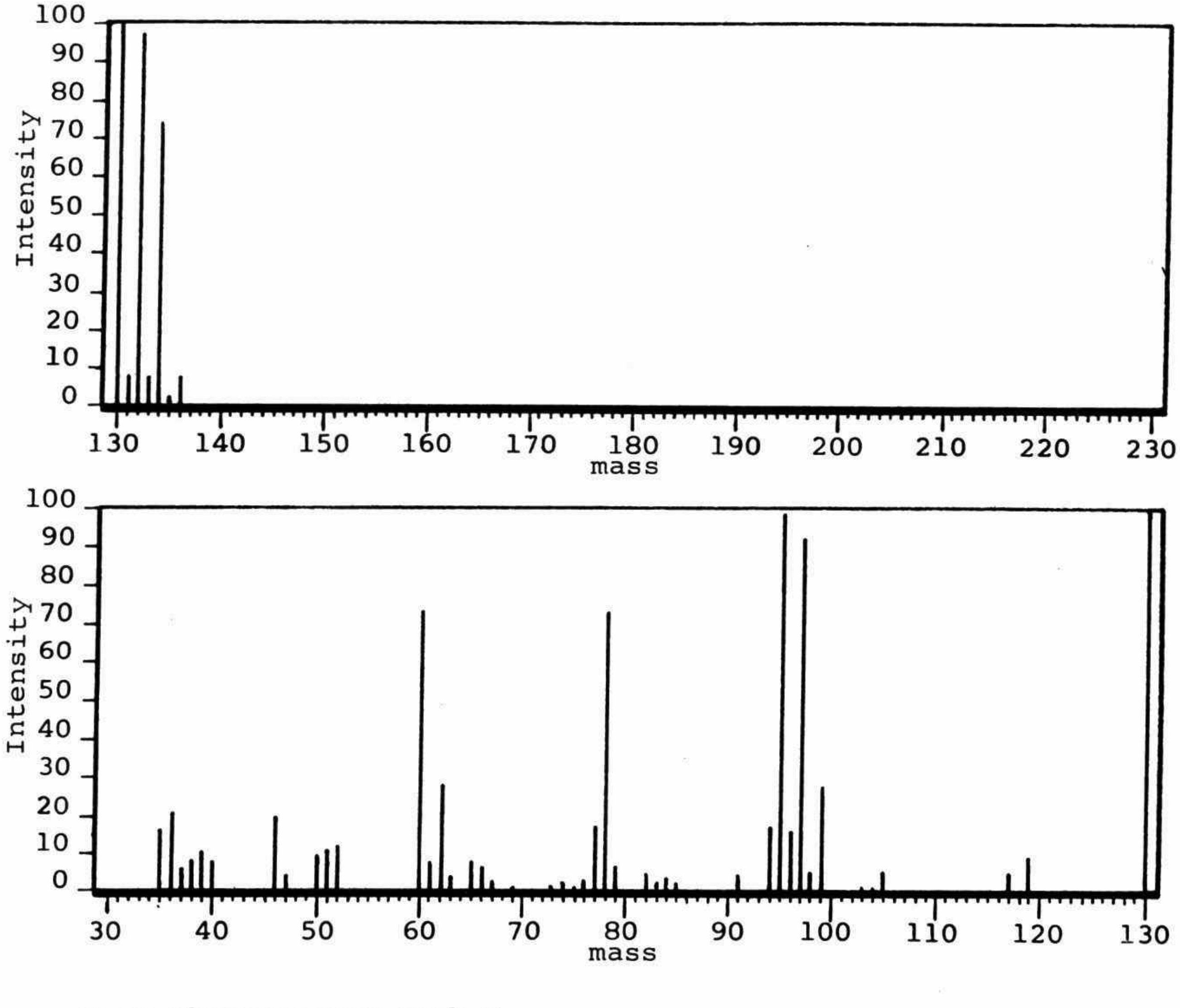
Figure 10: 1,2 DICHLOROETHANE



Mass Chromatogram Peak 6

Spectrum No. 102

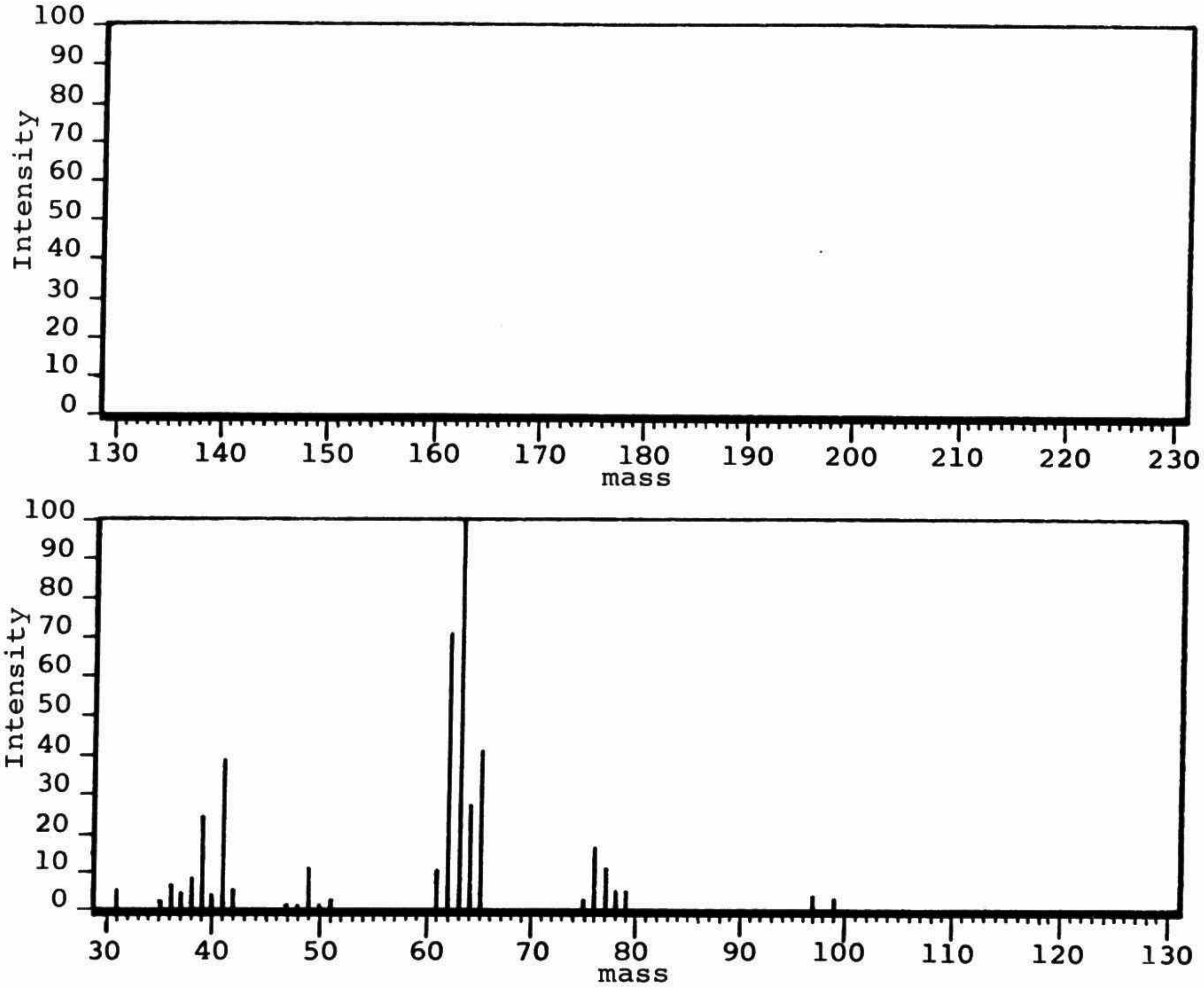
Figure 11: TRICHLOROETHYLENE



Mass Chromatogram Peak 7

Spectrum No. 116

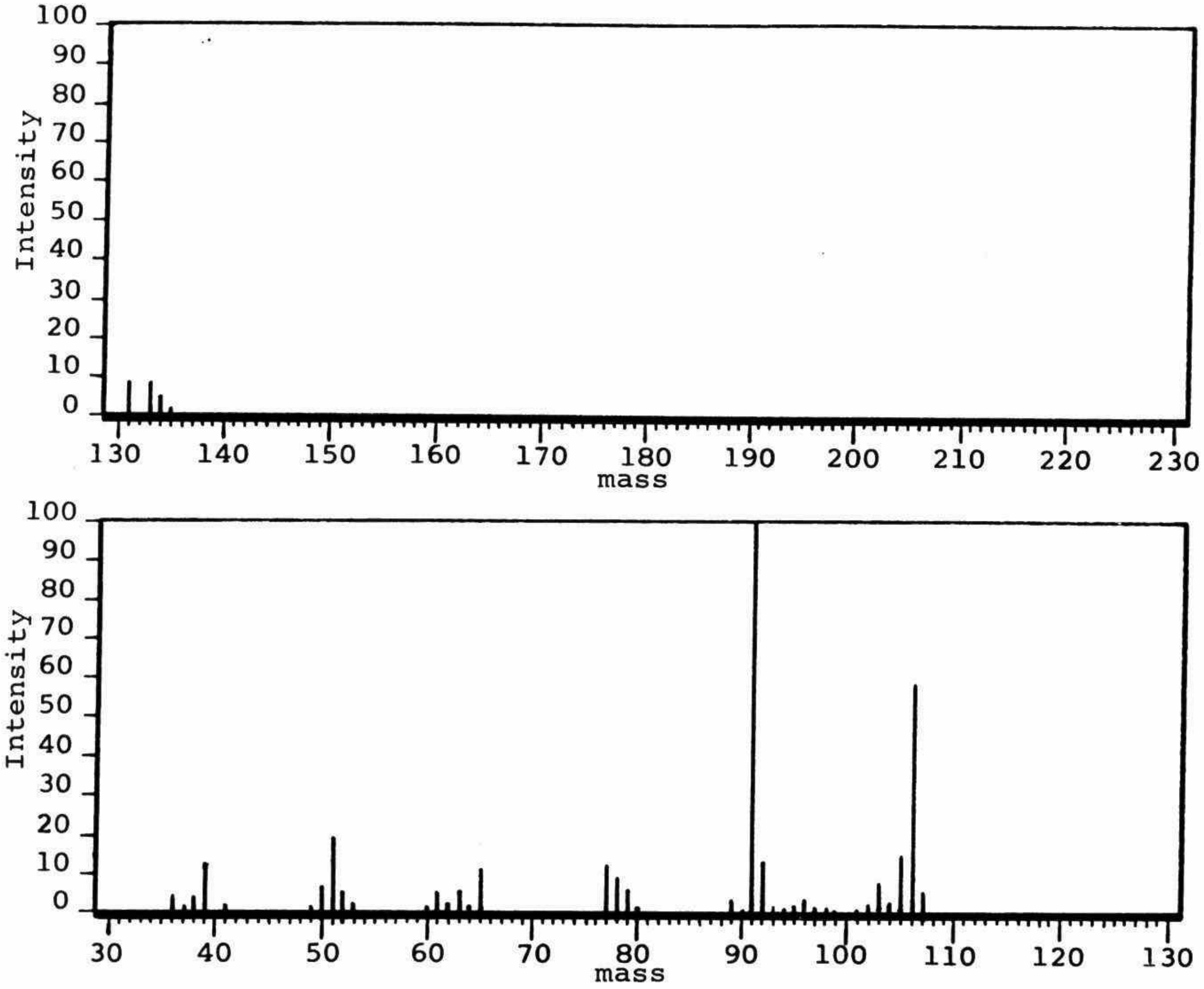
Figure 12: 1,2 DICHLOROPROPANE



Mass Chromatogram Peak 8

Spectrum No. 126

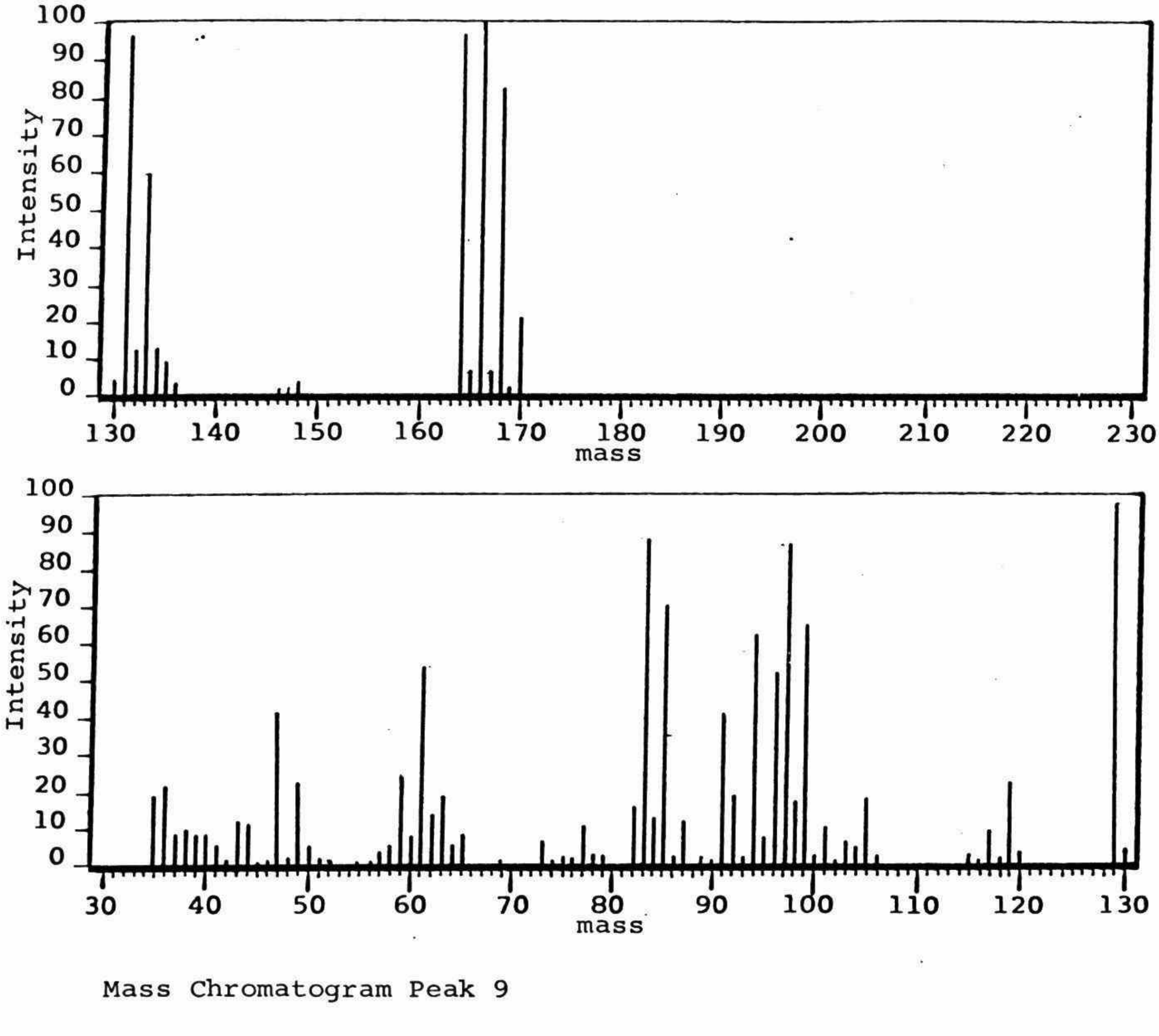
Figure 13: XYLENE



Mass Chromatogram Peak 10

Spectrum No. 189

Figure 14: TETRACHLOROETHYLENE



Mass Chromatogram Peak 9

Spectrum No. 146

TD
427
O7
D84
1977